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Technical Report

A NEW TYPE OF HETEROGENEOUS
CATALYST WITH ISOLATED
FE-RH DIATOMIC SITES

by

James J. Hickman, Jr.

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A NEW TYPE OF HETEROGENEOUS
CATALYST WITH ISOLATED
FE-RH DIATOMIC SITES

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James J. Hickman, Jr.



Technical Report No. TR 88-004

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← Certain rhodium-on-alumina catalysts were reinvestigated using a well-characterized rhodium-on-alumina catalyst as a reference. The reference catalyst contained "rafts" of eight to ten atoms. A concentration series with succeeding lower metal loadings was prepared. All these catalysts maintained the same selectivity for the test reaction but had successively lower rates. This was explained by claiming that rhodium atom sites were created, but were rendered inactive for the test reaction by either poisoning or dissolution into the alumina matrix.

Mossbauer Spectroscopy was used to characterize higher loading iron-rhodium catalysts. This spectroscopic method demonstrated that organometallic complexes do interact with supports in different manners depending on the solvent utilized. Also, effects were seen which suggested that hydrogen can influence particle morphology in iron-rhodium systems in a manner analogous to palladium hydrogen interactions. This method also demonstrated a sensitivity which would enable the examination of mono- and di-atomic iron containing sites if ^{57}Fe was employed.

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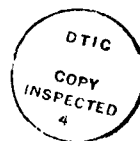
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ABSTRACT

A totally new type of heterogeneous catalyst was created containing iron-rhodium diad sites. These sites were totally different from traditional iron-rhodium alloy catalysts. They exhibited a constant selectivity and specific activity with the test reaction. These sites were prepared by the low temperature decomposition of an organometallic compound, $(CO)_3Fe(\mu-C_7H_7)RhCOD$, in a hydrogen atmosphere. The method of characterization employed involved the catalysts' selectivity towards the isomerization and hydrogenation of 1-butene. Catalysis was accomplished using a plug-flow differential microreactor at 30°C. These diad sites also appeared to be different from rhodium-only catalysts at mono-atomic dispersions.

Certain rhodium-on-alumina catalysts were reinvestigated using a well-characterized rhodium-on-alumina catalyst as a reference. The reference catalyst contained "rafts" of eight to ten atoms. A concentration series with succeeding lower metal loadings was prepared. All these catalysts maintained the same selectivity for the test reaction but had successively lower rates. This was explained by claiming that rhodium atom sites were created, but were rendered inactive for the test reaction by either poisoning or dissolution into the alumina matrix.

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Chapter I

INTRODUCTION

The first metal catalysts employed contained only unsupported metal particles. It was later shown that better metal efficiency and thus greater catalyst activity could be attained by placing the metal onto an inert, high surface area support such as silica, alumina, or diatomaceous earth. As this technology became more advanced, a wider variety of metals, metal combinations, and supports came into use. Investigators then postulated that putting smaller particles on these various supports would not only result in a greater metal efficiency due to increased metal site area but that different reactivity would result from the increase in defect sites.¹

The natural extension of this was to create a totally new type of site by placing metal atoms, diads, and triads on the support. However, no one was able to create these new sites because the only method of preparing highly dispersed catalysts was by ion exchange reactions,² and these catalysts invariably sintered to some extent during the high temperature reductions needed to reduce metal salts. Yermakov³ attempted to circumvent this problem by using organometallic complexes that decomposed readily at low temperatures, but the high metal loadings he studied yielded only metal aggregates.

However, Skell postulated that by the use of metal atom techniques which create organometallic compounds of low thermal

stability, and the use of sufficiently low metal loadings, these ultimate dispersions could be reached. Work by Kennan⁴, Niznik⁵, and Schwartz⁶ has shown that mono-atomic dispersions are plausible using this approach. The major problem encountered in their work involved the characterization of these sites. Most spectroscopic methods can not "see" these entities because of size and signal limitations. Consequently, the logical step was to take advantage of the hoped-for changes in reactivity and selectivity of the new sites. They showed that characterization can be achieved using the reaction of 1-butene with hydrogen.

The purpose of the present study was twofold. One direction was to prove that hetero-bimetallic diads could be created and that their reactivity was different from either component alone. The previous work had not demonstrated that a limit in selectivity and reactivity was reached, only that significant changes in selectivity and reactivity were possible. This study will use novel hetero-bimetallic complexes with low decomposition points to determine these reactivity limits and to examine the differences between catalysts containing rhodium only and iron-rhodium.

The second area of study was to see if iron could be used as a probe for Mössbauer Spectroscopy. This spectroscopic tool can be used to determine particle size at low temperatures and to elucidate the extent of the binding between the two metals.⁷ The Mössbauer effect can also determine the extent of the interaction of the iron with the support; this will reflect the interaction of the other metal in the diad which, in this study, will be rhodium.

Chapter II

STRATEGY

The catalysts to be examined were prepared by the low temperature reduction of organometallic complexes. These complexes were supported on carbon. The di-atomic sites were created by placing the complexes' molecules far enough apart so as to inhibit any site-to-site interaction during reduction or catalysis. This was to be accomplished by employing low loadings.

When one prepares di-atomically dispersed catalysts, the experimental difficulty presented lies in the catalyst characterization. Since di-atomic dispersions are most likely to exist at relatively low metal loadings⁸, one can not readily employ most of the common methods of physical characterization. The practical approach is to choose a suitable reaction and to compare the catalytic properties of the di-atomic system with well-characterized systems of known metal disposition. This can include catalysts of high metal loading, which are composed of metal crystallites, or catalysts of intermediate metal loading, which have been investigated using various techniques.^{9,10}

The principal method of characterization chosen for this study was a comparison of the relative rates of isomerization and hydrogenation of 1-butene. Rhodium is very active for this

reaction, so a wide range of metal loadings were compared under mild reaction conditions.¹¹ Also, since iron is not active for this reaction by itself,¹² iron-rhodium catalysts were compared to catalysts containing only rhodium, to observe the effect iron has on the ability of rhodium to catalyze this reaction. Thus, not only would the differences in selectivity from high metal loading to low metal loading be observed, but also how these selectivities differed from the selectivities reported for pure rhodium catalysts on various supports.

The reasoning behind using this method of kinetic characterization involved certain observations made by Boudart.¹³ He found that most reactions fall into two classes. One class he labeled "structure sensitive" or "facile"; these were reactions in which specific activity or selectivity is dependent upon factors such as the shape or size of the metal crystallites. The other class he referred to as "structure insensitive," whereby the selectivity and specific activity was unaffected by particle size. Therefore, in a structure insensitive reaction, the specific activity of a metal powder would have approximately the same specific activity as a highly dispersed supported metal.

At this point it is necessary to indicate the difference between specific activity or turnover number and the manner in which the rate values have been reported. The specific activity takes into account the number of sites actually available for

catalysis and is generally reported as $(\text{moles product}) \cdot (\text{moles surface atoms})^{-1} \cdot (\text{time})^{-1}$. The number of surface sites are usually determined using chemisorption.¹⁴ However, due to abnormalities encountered when chemisorption is attempted on the iron-rhodium system (see below), the dispersions of the metal in these catalysts cannot be determined with certainty except at the ultimate dispersions. Thus, the rates will be reported per mole of rhodium metal.

The reaction of 1-butene with hydrogen has been described as a "structure insensitive" reaction.¹³ This reaction remains primarily a hydrogenation reaction over a rhodium catalyst under mild conditions. However, theoretical arguments have suggested that small particles may exist in pentagonal, tetrahedral, or icosahedral forms rather than in the normal fcc structure.¹⁵ Other authors have suggested that "rafts" may form on the surface of the catalysts at lower metal loadings.¹⁶ These changes in metal structure may not only affect the geometry of the site; the electronic environment of each atom may begin to differ from its neighbors as well.¹⁷ The support may also begin to play an important role in catalyst behavior because most, if not all, of the metal will be in intimate contact with the surface. So, it is suggested that even a "structure insensitive" reaction may be influenced by these factors as the metal content on a support is lowered.

These factors could produce gradual changes in rate as well as in selectivity, as the particles become smaller and the normal metal structure is further distorted. Also, a limit should be reached when the particle cannot be made any smaller and is dependent on the catalyst precursor. A mono-atomic precursor should give atomic dispersions, a di-atomic support should give diatomic sites, etc. This limit should be indicated by a constancy in specific activity and selectivity; this would appear as a "plateau" as the changes in metal loadings are compared to the selectivity or activity of the probe reaction.

Another method of characterization is to use the iron as a probe for Mössbauer Spectroscopy. This spectroscopic method gives detailed information concerning the electronic environment in the immediate vicinity of the nucleus.⁷ By means of isomer shift and hyperfine splitting at various temperatures (typically 4°K, 77°K, or 273°K), the extent of interaction of the complex with the support may be observed as well as the degree of decomposition of the complex after reduction. The integrity of the original Fe-Rh bond may also be determined by comparing Fe only containing catalysts subjected to the same treatments. The hyperfine splitting due to the magnetic susceptibility of the particle may also be used to determine particle size.¹⁸ This is accomplished by varying the temperature and determining where the particles stop being superparamagnetic. This would give information involving

particle sizes at low loadings which are not possible with any other method available to this laboratory.

Chapter III

EXPERIMENTAL

Materials

Catalyst Precursor Compounds

The Fe-Rh hetero-bimetallic complex, $(\text{CO})_3\text{Fe}(\mu\text{-C}_7\text{H}_7)\text{RhCOD}$ (1), was prepared by A. Salzer¹⁹. The $(\text{CO})_3\text{FeC}_7\text{H}_8$ (2) was prepared using the method of Takets.²⁰ The $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (3) was used as received from the ALFA division of Ventron.

Solvents

All solvents, received at 99%+ purity, were distilled over Na/K alloy under a N_2 atmosphere and then degassed until the vapor pressure of the gaseous impurities was less than 1×10^{-3} torr. The water used was doubly distilled biologically pure grade which was freeze-thaw vacuum-degassed.

Supports

Aluminum Oxid-C (Degussa Corporation), a $100 \text{ m}^2/\text{gm}$ γ -alumina, was degassed in vacuum at 300°C for 15 hours before use in order to remove adsorbed water.

The carbon used was an acid washed Monarch 880 carbon black from Cabot Corporation. It was a $300 \text{ m}^2/\text{g}$ carbon black with 90 m^2/g of this surface are being in micropores. The acid washing removed the majority of mineral impurities from the carbon, which was then reduced to 1050°C for 15 hours in 20-40 ml/min flowing H_2

to remove oxygen and sulfur impurities.²¹ (Figure 3.1). All supports were stored under a helium atmosphere in a glove box.

Gases

All gases used in reactions were of ultra-high purity grade. 1-Butene (Phillips research grade, 99.9%+) was dried over molecular sieves (Linde 4A) and freeze-thaw degassed until the vapor above the liquid contained less than 1×10^{-3} torr impurities. Ultra-high purity hydrogen and helium (either MG Scientific or Linde, 99.999%) were used in catalyst runs and carbon purification. These gases were further purified by passing through Oxy-traps (Alltech Associates) and molecular sieve traps (Linde 4A) to remove any remaining oxygen or water impurities.

Catalyst Preparation

All catalyst manipulations were performed using inert atmosphere techniques to prevent exposure to possible poisons. This involved Shlenck and glove box techniques. The catalysts were prepared either by incipient wetness (high loadings) or adsorption methods (low loadings). All vacuum pumping was carried out through liquid nitrogen traps.

Adsorption Method

The adsorption method was used if a catalyst was made below a weight loading of 0.10% Rh. The method involved dissolving the desired amount of the complex in a solvent and then syringing the

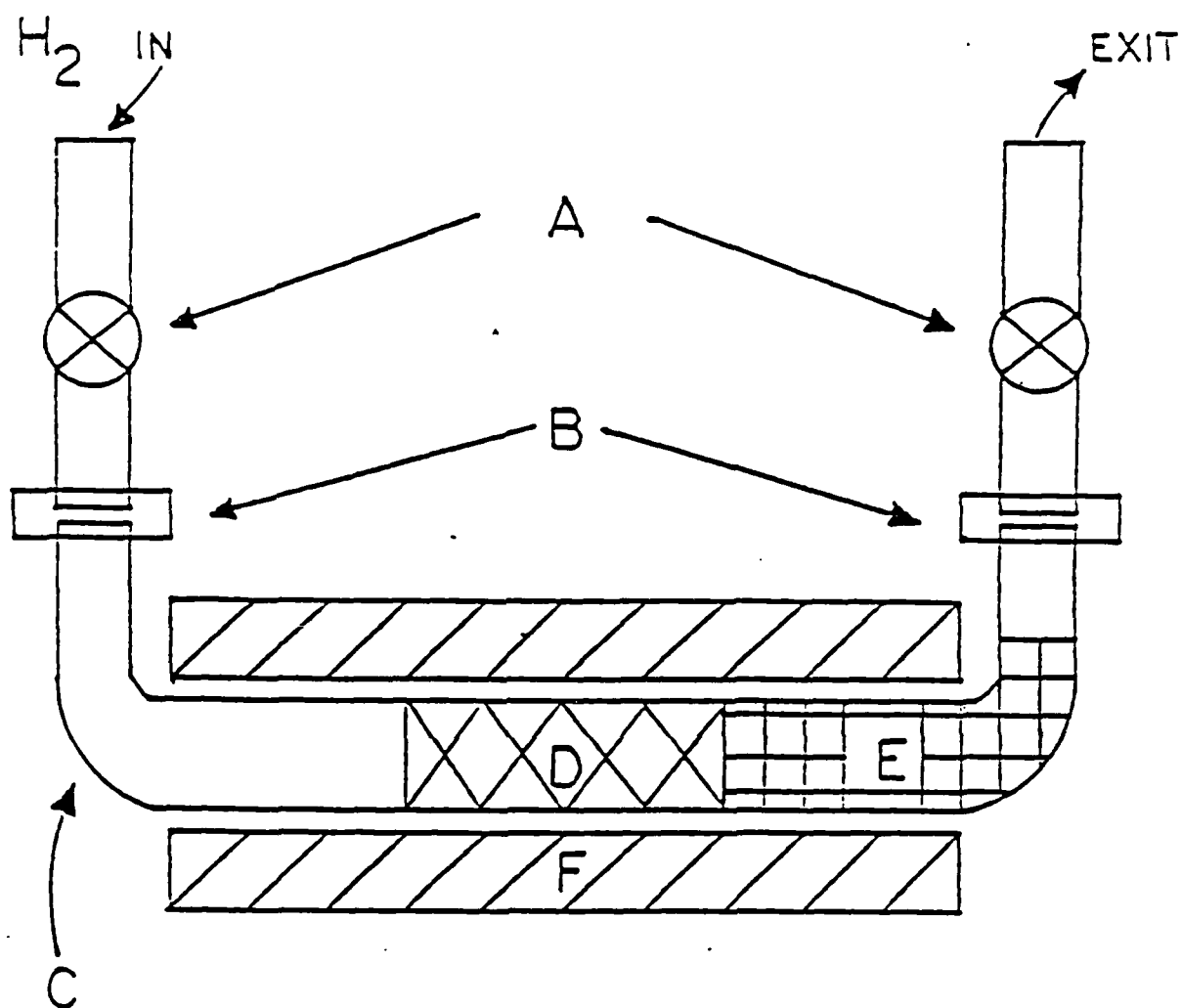


Figure 3.1. Apparatus Used for the Purification of Carbon

- A. Pyrex stopcocks
- B. Cajon fittings
- C. Quartz tube
- D. Carbon black
- E. Quartz wool
- F. Tube furnace

appropriate amount onto the support. If this amount of solvent was not sufficient to completely wet the support and allow for excess, then a sample of wet support was prepared (~3ml solvent per gram support) prior to addition of the organometallic sample so that the complex would spread evenly over the support during impregnation. With the catalysts prepared using pentane as the solvent, this interaction was maximized by lowering the temperature during the impregnation.

The solvent was removed by pumping until a pressure of less than 1×10^{-2} torr was reached. The sample was then stored under helium in a glove box.

Incipient Wetness

The solutions of the organometallic complexes used were all highly colored; this provided an excellent indication as to whether all the complex was adsorbed onto the support. If it was determined that not all the complex was adsorbed from solution, an incipient wetness technique was employed to prevent crystallization of the support on the flask walls during solvent removal. The metal complex was dissolved in the minimum amount of solvent necessary to wet the support. This solution was syringed onto the support. After stirring, the solvent was pumped off until the pressure reached 1×10^{-2} torr. The catalyst was stored under He in a glove box.

Metal Analysis

All catalysts were prepared from solutions which themselves were prepared using at least 20 mg of the complex. All weighings and volume determinations were measured to within $\pm 1\%$ so that the maximum error produced in the preparation of a catalyst was less than 5%. However, to verify this a number of samples were submitted to the Brezeale Nuclear Reactor for neutron activation analysis of Rh.

Neutron Activation

The standards used were a 1 wght % Rh and .1 wght % Rh on Monarch 880 prepared from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in aqueous solution. All samples were weighed into polyethylene vials with approximately the same volume. The vials were irradiated for 1 minute at a power output of 100 Kw. The samples were analyzed by counting the intensity of the γ -ray radiation emitted at 53 Kev with a Ge (Li) detector. The 53 Kev peak corresponded to the decay of Rh^{104} to Pd^{104} . The number of counts became a linear function of the rhodium concentration since the irradiation time and neutron flux were constant for both sample and standard. The rhodium concentration was then calculated from this relationship.

Catalyst Evaluation

Kinetics

These catalysts were evaluated for their ability to isomerize and hydrogenate 1-butene in the presence of excess hydrogen at low

temperatures (typically 30°C). The rates were determined with an atmospheric pressure, plug-flow, differential microreactor. The products were analyzed using a flame ionization gas chromatograph connected in series to a programmable integrator. A schematic of this reactor system appears in Figure 3.2. The gas mixture employed was a helium/hydrogen/1-butene (89:10:1) mixture at flow rates of either 50 ml/min or 100 ml/min. Helium was present as an inert dilutant to minimize heat and mass transfer effects. The 1-butene and hydrogen flow rates were determined using mass flow controllers (Brooks Instrument Co. Model #5850), which gave precise flow control ($\pm 1.0\%$ of full range) over a relatively wide range of interest. The helium flow rates were controlled using a micrometering valve and monitored with a soap-bubbler flow meter with a volume of 10 ml calibrated to $\pm .1$ ml.

In preparation for a catalyst run, the bed was thoroughly base- and then acid-washed and then loaded with between 0.3 and 0.4 gm of catalyst. The bed consisted of a small glass fritted U-tube which could be mounted on the catalyst line using two Cajon fitted 3-way ball valves. The catalyst was placed on the line and reduced at the desired temperature (usually for 2 hours) in 100 ml/min of H_2 . Generally, if a dilution was required, the catalyst was removed from the line, placed in the glove box, diluted to the required metal content with the appropriate carbon or alumina support, and replaced on the line in a new catalyst bed. In either case, the catalyst was then placed in a silicone-oil bath which was

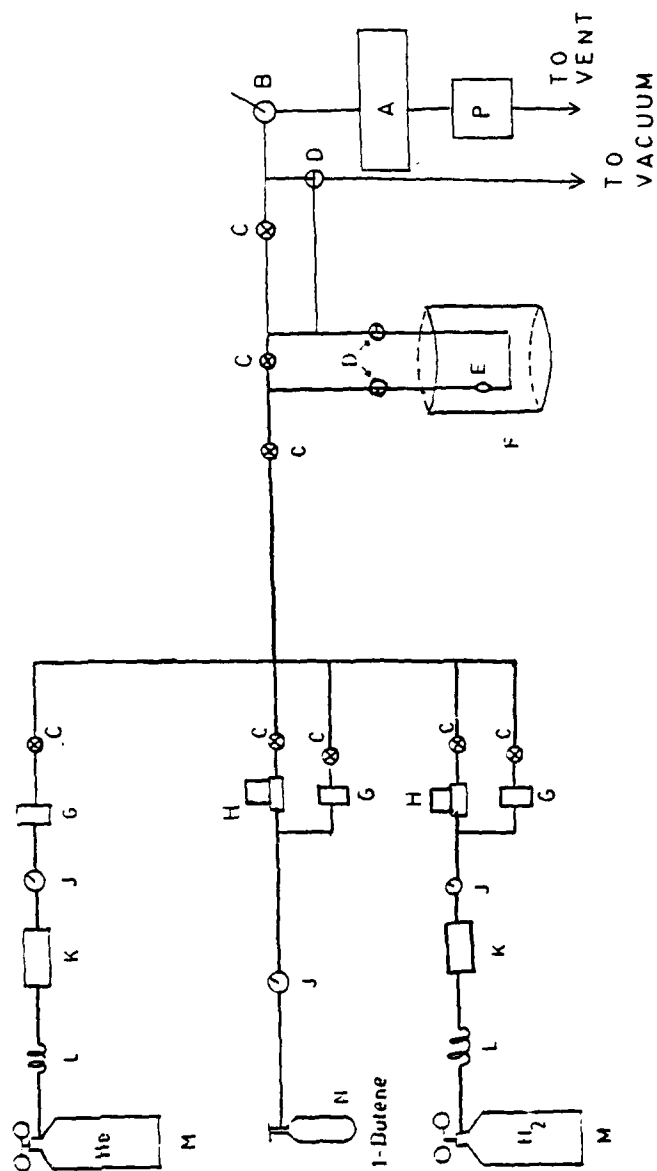


Figure 3.2. Plug-flow Differential Microreactor for the Reaction of 1-Butene with Hydrogen.

Figure 3.2. Continued

- A. Perkin Elmer Gas Chromatograph, Model F-11
- B. 6-way gas sampling valve
- C. Whitey shutoff valve
- D. Whitney 3-way ball valves
- E. Catalyst
- F. Silicone-oil bath
- G. Micrometering Valve
- H. Brooks Inst. Co. Mass Flow Controllers, Model 5850A
- J. Watts pressure regulator
- K. Molecular sieve trap
- L. Oxy-trap
- M. Ultrapure gas cylinder
- N. Pressure tube
- P. Hewlett-Packard Integrating Recorder, Model 3390

maintained at the desired reaction temperature, usually $30 \pm .1^\circ\text{C}$. The bath temperature was controlled at temperatures below 90°C using a YSI model 71A temperature controller with thermistor probe.

The reaction mixture was passed through the bed at the desired flow rate and the effluent gas sampled with a Supelco 6-way gas sampling valve. This allowed the gas to be analyzed chromatographically without disrupting the flow. The 1-butene, butane, cis-2-butene, and trans-2-butene were separated using a Perkin-Elmer Model F-11 gas chromatographer. The GC was equipped with a 30' x 1/8" packed column containing nitrile silicone polymer on acid-washed diatomite support (Supelco 23% SP 1700 on Chromasorb PAW) which was maintained at 60°C . The flow rate through the column was varied from 20 to 30 ml/min of helium. The areas of the peaks were determined with a Hewlett-Packard programmable, integrating recorder, Model 3390. The product areas were then reported as percent conversions of 1-butene. The retention times of the peaks varied with carrier gas flow rate and oven temperature, but good baseline separation was achieved in most cases.

The catalyst activity was generally monitored for 20 hours. Samples were taken frequently during the first 3-5 hours (every 10-20 minutes) and then periodically during the remainder of the run.

A typical catalyst exhibited sharp initial decreases in activity followed by a more gradual linear decrease in activity.

The rates were determined by plotting the percent conversion as a function of time and then extrapolating the linear region back to time zero. This method was found to be reproducible and gave an accurate indication of the catalyst's activity.

Mössbauer Spectroscopy

Two different Mössbauer cells were employed in this project in order to examine a wide variety of conditions. Both were in situ cells and were interchangeable with the remainder of the apparatus. One cell used x-ray transparent 131 Teflon Kapton (Dupont) windows; an almost identical cell is reported elsewhere.²² The cell was capable of operation at temperatures ranging from 77°K to 723°K and handled a sample size of up to five grams.

The second cell was included with an Air Products LT-3-110 Heli-Tran liquid helium transfer refrigerator. It was capable of operation from 0°K to 330°K and handled a sample size of up to one gram. The cells were attached to a standard glass vacuum/gas handling system. This allowed samples to be treated under vacuum conditions (1×10^{-6} torr) and at atmospheric pressure in various gas mixtures. The cells were loaded with catalyst samples under inert atmosphere in a glove box (Vacuum Atmospheres). The sample was contained between the cell windows by Grafoil sheets.

Constant acceleration spectra were obtained with an Austin Science Associates, Inc. S-600 Mössbauer Spectrometer, equipped with an electronic Doppler velocity motor. The source was obtained from New England Nuclear, Inc. and was 50 μ Ci of ^{57}Co diffused into

a palladium matrix. The pulses from the proportional counter detector (Reuter Stokes) were amplified, shaped and gated using Austin Sciences, Inc. electronics. Shaped pulses were sent to an Austin Science C-1 computer-based acquisition system. They were then sent to a laboratory IBM/PC to be stored on floppy discs or sent to the University mainframes, where they were analyzed using an improved version of the program MFTT.²³ All isomer shift values are reported relative to iron metal foil.

Adsorption Studies

These studies were to enable the calculation of specific activities and to give a reasonable estimation of the particle size of high loading catalysts. Iron does not chemisorb hydrogen at room temperature to any appreciable amount,²⁴ while hydrogen chemisorbs on rhodium in a one to one molar ratio at room temperature.²⁵ It was hoped that the dispersion of the catalyst could be determined from chemisorption of the hydrogen on rhodium only and the iron would act as an inert dilutant. The method and apparatus are described elsewhere⁴ and were followed exactly. Reductions were carried out at 100°, 150°, 200°, 250°, 300°, and 350°C. Chemisorption was performed on 0.85 g of a 0.51 wght % Fe-Rh/C catalyst after each reduction.

Catalyst Designation

This study involved a number of compounds and supports, whose combinations may be cumbersome and confusing. To facilitate

clarity, the catalyst formulations were abbreviated as follows:

Fe-Rh - an iron-rhodium abbreviation

Fe-Rh/C - the complex $(\text{CO})_3\text{Fe}(\mu\text{-C}_7\text{H}_7)\text{RhCOD}$ adsorbed on carbon.

If no reduction was yet performed on the catalyst, NR will follow the designation. If the catalysts were reduced, the temperature and conditions will be indicated.

Rh/C - the complex $\text{Rh}(\text{allyl})_3$ on carbon for kinetic comparisons

Rh/ Al_2O_3 - $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ on Degussa alumina

Fe/C - the complex $(\text{CO})_3\text{FeC}_7\text{H}_8$ on carbon for Mossbauer comparisons

- The solvents used will be noted in each section.

Another point involved the reporting of metal weight percents on catalysts for the Fe-Rh catalyst system. Iron is not known to be a catalyst for the reaction of 1-butene with hydrogen at low temperatures. So, to enable ready comparisons between Fe-Rh catalysts and catalysts containing rhodium only, all weight %s for the Fe-Rh system incorporated the amount of rhodium metal only. The rates were also be based only on the number of moles of rhodium present. The rate based on the total amount of metal present may be obtained if desired, by dividing the rhodium rate by two, because iron is present in a equimolar amount.

Chapter IV

RESULTS AND DISCUSSION

The catalysts examined were prepared to have either a Fe-Rh diatomic site or to have agglomerations of atoms as the active sites. The diatomic sites were prepared by a low temperature reduction of a hetero-bimetallic organometallic precursor. Since iron has no catalytic activity for the reaction to be studied, these catalysts were compared to rhodium-on-carbon catalysts examined previously.⁴ This gave indications as to whether the iron exerted a chemical influence on the rhodium in the di-atomic state. These catalysts were prepared in benzene and pentane because previous work had shown that high dispersions were possible with these solvents.⁴

The reaction studied examined the difference in relative rates of the hydrogenation and isomerization of 1-butene. High rates of isomerization relative to hydrogenation were a general indication of a molecularly defined site, while hydrogenation predominated in larger metal aggregates. A typical hydrogenation catalyst is represented in Figure 4.1, and a general representation of an isomerization catalyst is plotted in Figure 4.2. The rates can be used to determine qualitative differences in active sites as well.

An attempt was also made to show that mono-atomic rhodium sites are formed on alumina. Some catalysts previously characterized using other methods²⁶ will be examined by the reaction kinetics outlined previously.

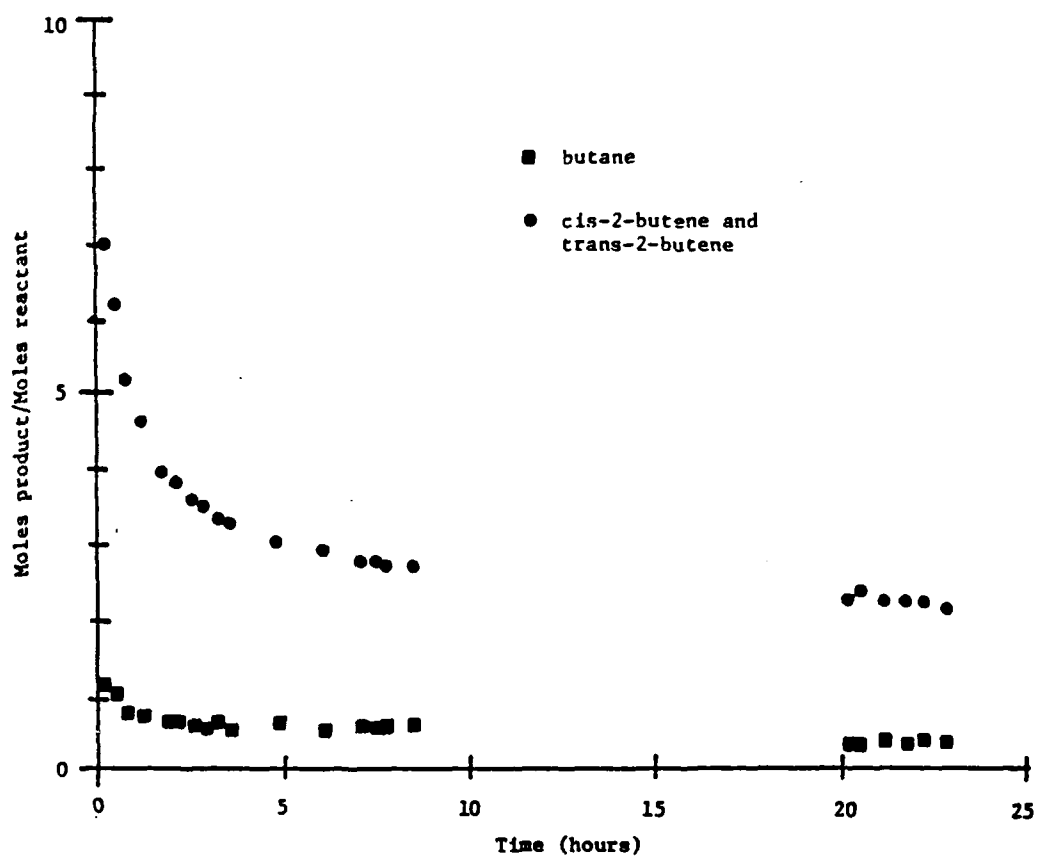


Figure 4.1. Typical Isomerization Catalyst. 0.006 wght % Rh, Fe-Rh/C Reduced at 125°C in Hydrogen.

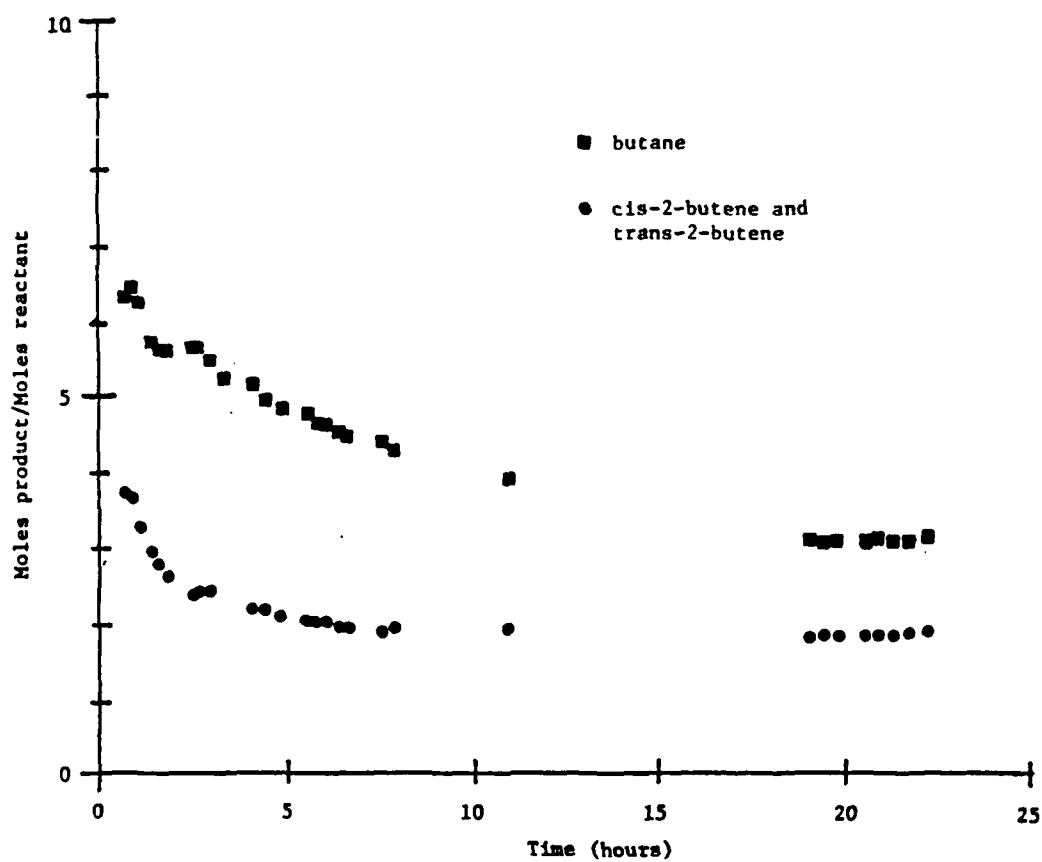


Figure 4.2. Typical Hydrogenation Catalysts at 30°C. 0.98 wgt % Rh, Fe-Rh/C Catalysts, diluted to .00035 wgt % Rh with carbon, after 125°C reduction in hydrogen.

Mössbauer spectroscopy was used to indicate catalyst reduction steps. The temperature effect on hyperfine splitting was examined to see if particle size could be determined. Chemisorption was run on a select few catalysts.

Kinetics

Catalytic activity for the isomerization and hydrogenation of 1-butene was determined in a single pass differential reactor at 300°C. Since the products were present in low concentrations, were continually removed from the system, and were not noticeable poisons to the reaction, they did not enter the rate expression. If the reaction was carried out in the differential mode, the hydrogen and 1-butene concentrations would remain essentially constant and concentration gradients would not be present as the gases passed through the catalyst. This would simplify data analysis and allow calculation of rates from equation 4.1,²⁷

$$r = F \cdot dx \quad (4.1)$$

where r = the rate expressed as (moles products) \cdot (moles metal⁻¹) \cdot (hour)⁻¹; F = the feed rate of 1-butene, typically 2.3×10^{-3} moles \cdot hour⁻¹; dx = the differential conversion (percent conversion/100).

The limit of maximum conversions allowable, which would not invalidate equation 4.1, was about 10%. Assuming a linear decrease in 1-butene concentration throughout the bed, this gave an average apparent feed rate of .95 ml/min and introduced an error of approximately 5% in the final rate calculation. Since absolute

rates were not the primary interest in this investigation, but only selectivities and the relative differences in rate, this error was acceptable. However, the definition of a differential reactor requires that conversion be maintained at a level low enough to prevent gradients due to diffusion. Since the 10% limit quoted earlier was higher than normally utilized in a differential reactor,²⁸ an experiment was conducted to demonstrate that the kinetics are valid to a limit of approximately 10% conversions.

In an integral reactor, changes in the space velocity (bed volume \cdot flow rate⁻¹) would produce observably different kinetics in a reactor.²⁸ This should not have an effect in a differential reactor over reasonable ranges of space velocity. The flow rates utilized in the reactor were generally 100 ml \cdot min⁻¹ but were occasionally 50 ml \cdot min⁻¹ to accommodate very inactive catalysts. If one were to vary the flow rate of all the compounds in the feed stream to produce overall conversions throughout a range of 1-10% and the rates did not change, it could be assumed that in this range and for these conditions a differential mode existed. This experiment was performed and the following results are listed in Table 4.1. These results indicated rates which were constant within experimental error; so for this reaction, under these conditions, diffusional limitations were neglected.

Table 4.1

Validation of Differential Mode in Experimental Range

He	Flow Rates ^a		Total % conv.	b r_H	c r_T	d r_C	e I/H
	H ₂	1-butene					
178.0	20	2.0	9.02	5.50	1.95	1.44	0.62
89.0	10	1.0	4.51	5.43	1.99	1.48	0.64
44.5	5	0.05	2.29	5.49	2.05	1.50	0.65

a The flow rates are in $\text{ml} \cdot \text{min}^{-1}$.

b Rate of hydrogenation in mole product $\cdot \text{moles Rh}^{-1} \cdot \text{hr}^{-1} \cdot 10^{-3}$.

c Rate of isomerization to trans-2-butene in moles product $\cdot \text{moles Rh}^{-1} \cdot \text{hr}^{-1} \cdot 10^{-3}$.

d Rate of isomerization to cis-2-butene in moles product $\cdot \text{moles Rh}^{-1} \cdot \text{hr}^{-1} \cdot 10^{-3}$.

e Selectivity, $r_I \cdot (r_C + r_T)^{-1}$

Reaction Orders

The reaction orders of hydrogen and 1-butene were determined, assuming a rate law of the form of equation 4.2,

$$r = K e^{E_a/RT} [\text{butene}]^N [\text{H}_2]^M \quad (4.2)$$

by varying one parameter and holding the remainder constant.¹⁴

This was important, not only to reveal details of this reaction over a Fe-Rh catalyst, but also for comparison to the data obtained with Rh-only catalysts. The reaction order of each component was determined by taking a fresh catalyst, reducing it in H₂ at 125°C, and then monitoring conversions at 30°C. When the catalyst had reached a steady state condition, the flow rates were varied over the desired ranges. For hydrogen this range was from 2 ml·min⁻¹ to 20 ml·min⁻¹ in increments of 2 ml·min⁻¹ and for 1-butene it was from 0.5 ml·min⁻¹ to 3.0 ml·min⁻¹ with an arbitrary step. The reaction order of each product was then determined graphically. They are listed in Table 4.2 along with comparable data of some Rh-only catalysts.

An important point to note is that the butene order was constant over the entire range of testing for each product; however, for all three products in the hydrogen reaction order determination, the order approached zero as the extremes of H₂ flow were reached. However, the relationship was linear in the region of catalytic study.

Another feature was that the orders for the Fe-Rh catalyst were different from the Rh-only catalysts. An important aspect was that both the hydrogenation and isomerization products had negative

Table 4.2

Reaction Orders of Some Rhodium Containing Catalysts

$$r = Ke^{E_a/RT}[1\text{-butene}]^N[\text{H}_2]^M$$

Catalysts	Hydrogenation		Isomerization	
	N	M	N	M
A	-0.03	0.80	-0.27	0.13
B	-0.41	1.20	-0.43	0.81
C	0.00	1.00	-0.40	-0.10

A 0.009 wght % rhodium on Monarch 8804

B 0.98 wght % rhodium, Fe-Rh/C

C 1.07 wght % rhodium on SiO₂⁴

orders in butene. This probably can be attributed to a shift in the equilibrium of the desorption of products from the active site at higher olefin concentrations, because 1-butene is not an irreversible poison for this reaction.

Activation Energies

The activation energies were determined by holding the concentrations of the reactants in equation 4.2 constant and varying the temperature. A 0.006 wght % Rh (Fe-Rh/c) catalyst was run at 20, 40, and 50°C. The data at each temperature was determined with a fresh catalyst after a 125°C reduction in hydrogen. The activation energies are listed in Table 4.3 and compared with those of catalysts containing rhodium only on various supports. These activation energies also suggested that there were no major diffusion factors involved in this study, because activation energies for diffusional processes are less than 2 Kcal/mole.

Fe-Rh/C Catalysts on Carbon Prepared using Pentane

Previous work has shown that a well-dispersed catalyst can be prepared from a low temperature adsorption.⁴ This method employs pentane as the solvent and hydrogen pacificated carbon as the support. It was determined that the complex $(CO)_3Fe(\mu-C_7H_7)RhCOD$ was soluble in pentane and a low loading (0.015 wght % Rh)

Table 4.3

Activation Energies of Various Rhodium Containing Catalysts

Catalyst	Hydrogenation Ea (Kcal/mole)	Isomerization Ea (Kcal/mole)
A	9.2	9.7
B	8.1	8.4
C	7.3	9.0
D	8.5	10.0

A 0.006 wght % rhodium, Fe-Rh/C

B 0.009 wght % rhodium on Monarch 8804

C 1.07 wght % rhodium on SiO₂⁴

D 5.0 wght % rhodium on SiO₂¹¹

catalyst, Fe-Rh/C, was prepared. After a 125°C reduction in H₂, the catalyst showed no activity at 30°. Since it had been determined by spectroscopic methods (see below) that the complex is reduced under these conditions, insufficient metal loading was thought to be the problem.

A new catalyst was prepared to a 0.056 wght % Rh loading, and this only exhibited hydrogenation activity after a 125°C reduction in hydrogen. An interesting development, however, was an induction period in the catalyst activity, which showed that the catalyst activity grew under reaction conditions. A catalyst (0.056 wght % Rh, Fe-Rh/C) was reduced in a 99:1 (H₂/1-butene) mixture at 100 ml/min for 45 min and then in 100 ml/min hydrogen for an additional 45 minutes to clean the surface. This produced an active catalyst, albeit, a poorly dispersed hydrogenation catalyst.

A high loading catalyst (0.51 wght % Rh, Fe-Rh/C) was then prepared for a rate comparison to see if this catalyst was being poisoned or was just not very active. After reductions in hydrogen only and hydrogen and 1-butene at 125°C it was determined that the overall activity was better than the low loading. Also, the reduction within the olefin produced a more active catalyst. However, the overall rates were much lower than the rates reported for Rh/C catalysts made from Rh(allyl)₃ in pentane. To determine if a higher reduction temperature would clean the surface and create a more active catalyst, additional samples were reduced, using both reduction methods, at 200°C. Surprisingly, both methods

produced very inactive hydrogenation catalysts. All catalyst runs appear in chronological order in Table 4.4.

A few additional catalysts were attempted at low loadings, but they all produced poorly dispersed hydrogenation catalysts. A possible explanation is that the metal particles were incorporating carbon fragments and that this altered the nature of the active sites. Kabunde has shown that this may cause significant alterations in activity and selectivity.²⁹ Another possible explanation is that the complexes' solubility in pentane dropped dramatically with decreasing temperature. The solvent was removed at -40°C during the impregnation, possibly causing the deposit of crystallites on the support rather than promoting interaction with the support. This would result in the formation of large particles that would be difficult to reduce. In any case, they would definitely be hydrogenation catalysts. The logical step at this point was to try a solvent in which the complex was highly soluble. Since benzene had been used to produce well-dispersed catalysts previously and did not require a low temperature step, it was the next choice for an impregnation study.

Fe-Rh/C Catalysts Prepared using Benzene

The failure to achieve well-dispersed catalysts when using pentane as the solvent illustrates that each complex can interact differently with the various solvents and supports available. Kennan⁴ had previously found that even temperature and solvent functionality affected the type of catalyst produced. For years

Table 4.4

Catalytic Properties of Fe-Rh/C at 30°C
Prepared from $(\text{CO})_3\text{Fe}(\mu\text{-C}_7\text{H}_7)\text{RhCOD}$ in Pentane^a

Rh Metal loading, %	Reduction ^b Conditions	c r_H	d r_I	e r_T	f I/H
0.015	125° H ₂	NO OBSERVABLE RATE AT 30°			
0.056	125° H ₂	272	—	(272)	—
0.056	125° H ₂ +1-b	347	87	434	.25
0.51	125° H ₂	1146	344	1490	.30
0.51	125° H ₂ +1-b	1750	560	2310	.32
0.51	200° H ₂	299	141	440	.47
0.51	200° H ₂ +1-b	301	87	388	.29
0.061	125° H ₂	253	91	344	.35
0.061	125° H ₂ +1-b	358	90	448	.25
0.008	125° H ₂ +1-b	NO OBSERVABLE RATE AT 30°			

^a The catalysts appear in the chronological order in which they were run. All catalysis at 30°C.

^b Reductions were carried out at the temperature indicated in 100 ml/min of flow. Hydrogen:1-butene was 99:1.

^c Rates of hydrogenation moles product·moles Rh⁻¹·hr⁻¹.

^d Rate of isomerization in moles product·moles Rh⁻¹·hr⁻¹.

^e $r_I + r_H$

^f Selectivity, r_I/r_H

aqueous impregnations were favored over organic impregnation because ion-exchange was the only method of achieving high dispersions with the various supports. This history shows that in organic impregnations the interactions between solutes, solvents, and surfaces are not well understood and that the more broad based the catalytic study, the better the chance of success.

The complex, $(CO)_3Fe(\mu-C_7H_7)RhCOD$, demonstrated a much better solubility in benzene than in pentane. A low loading Fe-Rh/C test catalyst was prepared from a room temperature adsorption. This catalyst was predominantly active for the isomerization of 1-butene rather than the hydrogenation after a 125°C reduction in hydrogen. A reduction in 1-butene and hydrogen slightly reduced the hydrogenation activity but did not increase the overall rate. Knowing this, a concentration series was prepared using 1 as the precursor and carbon as the support. The concentrations ranged from a 0.98 wght % Rh, Fe-Rh/C to a 0.0003 wght % Rh, Fe-Rh/C. The number of catalysts prepared were heavily weighted to the low loadings to determine if a constancy was attained. All catalysts were reduced in hydrogen at 100 ml/min for two hours. The results of this series are presented in Table 4.5.

The ratio of isomerization to hydrogenation in this series clearly demonstrated that the catalyst has one type of active sites with loadings in excess of 0.1 wght % Rh, undergoes a transition between 0.10 and 0.01 wght % Rh, and has a distinctly different type of activity at loadings less than 0.01 wght %, constant down

Table 4.5
Rates of Catalysis of Fe-Rh/C at 30°C
Prepared using Benzene.

Rh Metal loading, %	Reduction ^a Temperature	^b r_H	^c r_I	^d r_T	^e I/H
0.98	125°	10655	4940	15600	0.46
0.98	125°	12800	10300	23100	0.80
0.39	125°	3157	2160	5320	0.69
0.10	125°	1170	1470	2640	1.25
0.05	125°	220	508	728	2.30
0.025	125°	199	558	727	2.80
0.011	125°	139	580	719	4.20
0.008	125°	73	488	561	6.80
0.006	125°	59	374	433	6.40
0.004	125°	75	467	542	6.30
0.004	125°	66	374	478	5.50
0.002	125°	58	377	435	6.50
0.0008	125°	32	195	227	6.10
0.0003	125°	26	166	192	6.40

^a All reductions were for two hours in 100 ml/min hydrogen.

^b Rate of hydrogenation in moles product·mole Rh⁻¹·hr⁻¹.

^c Rate of isomerization in moles product·mole Rh⁻¹·hr⁻¹.

^d $r_H + r_I$

^e Selectivity, r_I/r_H

to 0.0003 wght %, the lowest loading examined. This trend is best illustrated in Figure 4.3. The fact that even the specific activity remained constant in the low loading region indicated that no further changes occurred. The slight reductions in rate for the two lowest loadings may indicate the presence of some deactivation sites on the carbon. Poisons which only affected a small number of sites in the higher loadings can deactivate at low loading a larger percentage of the metal. A higher temperature reduction (200°C) of a high loading and a low loading catalyst showed that no significant further reduction occurred.

The dramatic increase in selectivity and the decrease in rate with decreasing metal loading strongly indicate that the Fe-Rh diatomic site is a totally different catalyst for this reaction than the bulk Rh-Fe alloy. It suggests that the larger the alloy particle, the more active the catalyst at the higher loadings. In the transition range, the mixture of sites leads to an average of rates, while the diatomic sites are a constant entity. It should be stressed that the majority of this decrease is caused by a 100-200x reduction in hydrogenation activity, which is normally associated with large particles. The plateau of constant specific activity proves that diatomic sites are the only species present at these loadings. The sites are still diatomic because Mössbauer spectroscopy has proved that the Fe-Rh diad does not separate (see below). It is also interesting to note that these changes occur below the metal range that has been fully characterized. This may

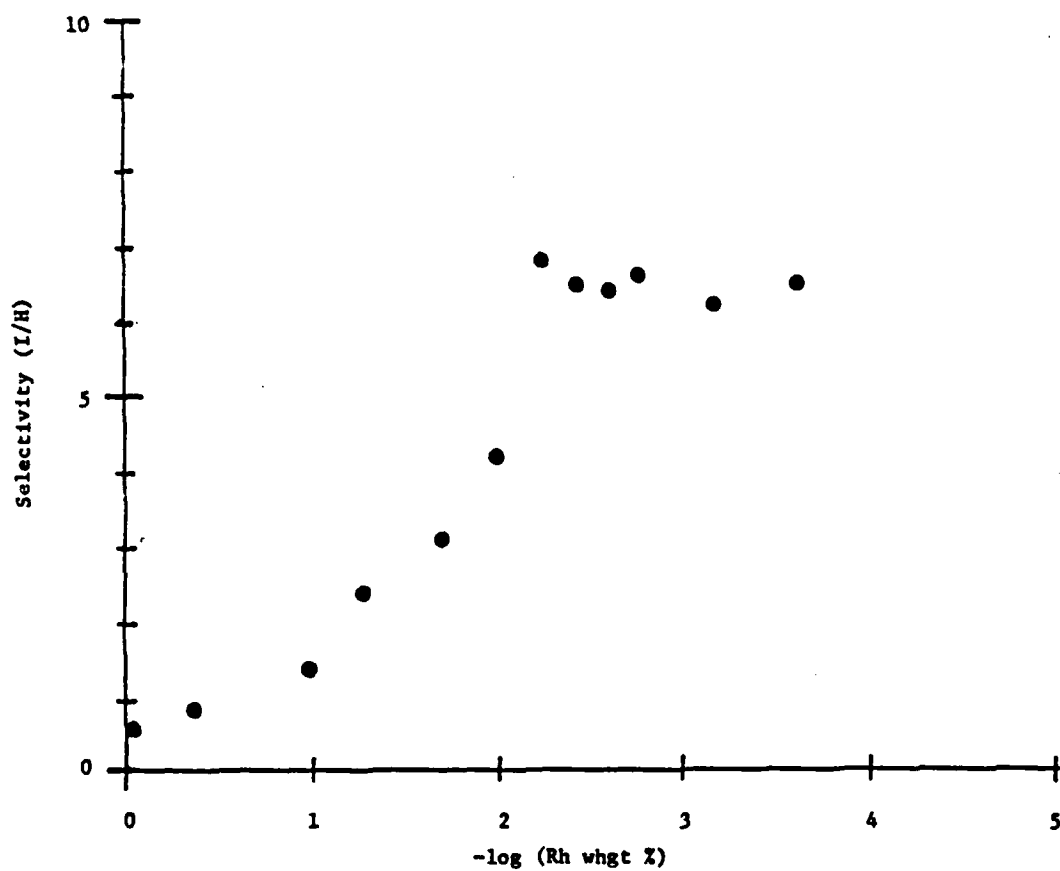


Figure 4.3. Plot of Selectivity vs. $-\log (\text{wght \% Rh})$ in the Fe-Rh/C concentration series.

be the reason no one has reported these ultimate dispersions before.

The Fe-Rh/C catalysts were also compared to a series of catalysts containing rhodium only. These were prepared from $\text{Rh}(\text{allyl})_3$, using benzene as the solvent, on Monarch 880 carbon. The catalysts were evaluated using the same methods employed in this study. It is very interesting to note that the Rh/C and Fe-Rh/C high loading catalysts are of similar activity and selectivity, but the low loading catalysts are different from one another (Table 4.6). The rhodium mono-atomic site differs from the Fe-Rh di-atomic site not only in reactivity but in ultimate selectivity as well. This indicates that not only can the monoatomic and hetero-bimetallic diatomic sites produce a catalyst different from bulk metal crystallites but that they can be different from one another even though their bulk phases are catalytically similar.

These differences between bulk properties and mono- and di-atomic properties are probably due to the ability of the smaller entities to have a stronger interaction with the support.³¹ This is analogous to work that had shown that "rafts" of metal particles exist on these supports under catalytic conditions and that each metal atom is in intimate contact with the support.³¹ Thus, close proximity can vary the properties of the metal atoms in the rafts much the same as varying the ligands in a homogeneous catalyst can radically change its activity and selectivity.³² Since the mono- and diatomic sites are less restricted than "rafts," the extent of

Table 4.6

Relative Reactivities of Rh/C and Fe-Rh/C Catalysts Prepared using Benzene

(CO) ₃ Fe(₁₁ -C ₇ H ₇)RhOOD on Monarch 880											
Rh(allyl) ₃ on Monarch 880											
Rh metal loading, %	Reduction ^a temperature, °C	c r _H	d r _I	e r _T	f I/H	Rh metal loading, %	Reduction ^b temperature, °C	c r _H	d r _I	e r _T	f I/H
0.98	RT	7.2	1.9	9.1	0.26	0.98	1250	11	4.9	16	0.46
0.98	100°	7.9	3.0	11	0.38	0.98	200°	13	10	23	0.80
0.12	RT	1.8	0.61	2.4	0.34	0.10	1250	1.2	1.5	2.6	1.3
0.010	RT	0.05	0.26	0.31	5.4	0.011	1250	0.14	0.58	0.72	4.2
0.007	RT	0.06	0.78	0.84	13	0.006	1250	0.06	0.37	0.43	6.4

^a Reduction in 100 ml·min⁻¹ H₂ for 1 hour.^b Reduction in 100 ml·min⁻¹ H₂ for 2 hours.^c Rate of hydrogenation in moles product·moles Rh⁻¹·hr⁻¹·10⁻³ at 300°C.^d Rate of isomerization in moles product·moles Rh⁻¹·hr⁻¹·10⁻³ at 300°C.^e r_I + r_H^f Selectivity, r_I/r_H

their interaction would be to a much greater degree. Consequently, it is reasonable to assume that a rhodium atom and a rhodium-iron diad can be very different from their bulk counterparts and each other. In a related experiment, the complex 1 failed to react with hydrogen in solution while $\text{Rh}(\text{allyl})_3$ readily decomposed to metal. Since changing the ligands will change a catalyst's properties in a homogeneous system, the addition of another different metal atom should alter the catalyst even more dramatically. This helps explain the difference in the Rh/C and Fe-Rh/C sites at their ultimate dispersions. The bulk alloy can probably establish some short range order which resembles the rhodium metal, but this is impossible with the diad.³³

Further Characterization of Rh/Al₂O₃ Catalysts

Previous work in this laboratory has shown that ultimate dispersions can be created on alumina with $\text{Rh}(\text{allyl})_3$.⁴ The catalysts, however, were found to be inactive for the hydrogenation and isomerization of 1-butene. But, various investigators have claimed that mono- and di-atomic sites are not stable and will not be formed.^{16,34,35} They have used various methods of characterization to prove their assertions such as TEM, EXAFS, and surface studies. In all cases, however, the metal loadings studied were in the ranges where we have found only "bulk" metal properties. If atom or diad sites exist at these loadings, they are probably in the minority and their detection would be obscured by the larger entities. So, if indeed mono-atomic sites are not

possible on an alumina surface, one should be able to take a well-characterized Rh/Al₂O₃ catalyst, such as Yate's rhodium on Degussa alumina, and do a concentration series without any changes in activity or selectivity.

D. C. Yates was contacted and he graciously supplied two Rh/Al₂O₃ catalysts prepared to specifications put forth elsewhere²⁶. Two more Rh/Al₂O₃ catalysts were prepared in this laboratory according to those techniques. All four catalysts were reduced according to his exact specifications to produce "rafts;" and their activities and selectivities were checked. These results are listed in Table 4.7.

These results show that the "rafts" have a selectivity of about 3.0 and that the selectivity is maintained all the way down the concentration series. However, the rate decreases by two-fold. If there was a selectivity change, this could be explained by changes in the active sites; but, since an eight atom raft is supposed to be the smallest stable entity possible, there should not be an activity decrease.

These observations can be explained in the following manner. The calculation which showed that atoms were not as stable as rafts was done using the surface as a model.³³ It did not take into consideration the possibility of rhodium atoms diffusing into the Al₂O₃ matrix and occupying vacant octahedral and tetrahedral holes. This idea has already been invoked to explain the deactivation of nickel on alumina catalysts.³⁶ Also, it has been shown that

Table 4.7
Catalytic Evaluation of Rhodium on Al_2O_3

Rh metal loading, %	Reduction ^a temperature, °C	^b r_H	^c r_I	^d r_T	^e I/H
0.2	200	423	1445	1868	3.4
0.02	200	99	251	349	2.6
0.008	200	57	170	227	3.0
0.002	200	25	78	103	3.1

^a Reductions were in 700 ml/min⁻¹ hydrogen after being ramped at 20°C per minute.

^b Rate of hydrogenation in moles product·moles Rh⁻¹·hr⁻¹.

^c Rate of isomerization in moles product·moles Rh⁻¹·hr⁻¹.

^d $r_I + r_H$

^e Selectivity r_I/r_H

rhodium, at its ultimate dispersion on alumina, is not an active catalyst for the reaction of 1-butene with hydrogen.⁴

Thus, the observations with the Rh/Al₂O₃ catalysts are explained easily. The eight atom "rafts" catalyze the test reaction with a selectivity of three and at a certain activity. Probably, some single atoms are present within the alumina matrix, but their signals are overwhelmed by the other forms of rhodium present. As the metal loading is decreased, the proportion of rafts to single atoms decreases as does the activity of the catalyst. The single atom sites are inactive; the selectivity does not change because the rafts are the only active species. This continues until the ultimate dispersion is reached as well as a totally inactive catalyst.

This experiment shows that the creation of mono- and di-atomic sites is not in disagreement with the previous work done on these catalysts. The characterization and assumptions put forth are all reasonable and just depend on the range of metal loading one is considering.

Absorption Studies

The results of the chemisorption experiments indicated a maximum of dispersion after the 250°C reduction. This is highly irregular, as higher temperatures generally cause sintering and redispersion of rhodium is not known to occur. Also, other sources of characterization have shown that complete reduction of the complex occurs after a 100°C treatment in hydrogen (see below).

It is suspected that either the two metals have alloyed, and a totally new set of experiments must be done to describe this system, or that some other source is acting as a hydrogen sink. This development makes the calculation of specific activities and related data irrelevant. Since this study is primarily concerned with characterization of low loading catalysts, and chemisorption with these systems is prohibitive due to equipment limitations, this method of characterization was abandoned.

Mössbauer Spectroscopy

One of the major drawbacks in studying mono-atomic and di-atomic sites is that most characterization techniques can not detect them on a support surface. One of the advantages of the Mössbauer Effect is that only certain atoms are Mössbauer active and the source used will dictate the atom studied. In this study, iron was included in the catalyst diad not only because it is an interesting catalytic metal but because it is Mössbauer active. Not only will this enable the environment around the iron atoms to be determined but also that of the rhodium atoms.

The primary information sought by using this probe was the determination of particle size. Zero valent iron, with a particle size of less than 200 Å, is superparamagnetic at room temperature.³⁷ This causes the spectrum to appear as a singlet centered approximately at zero Doppler velocity. As the temperature of the particle is lowered, the magnetic field vectors begin to orient themselves and a sextuplet will be formed from the

hyperfine field splitting, accompanied by an appropriate decrease in the singlet intensity. The temperature at which this hyperfine field appears can be used to interpret the spectrum in terms of particle size.⁷ Other investigators have claimed to have seen monoatoms, diads, and triads using Mössbauer Spectroscopy.³⁸ They isolated atoms in a frozen matrix and performed studies at less than 4°K, and claimed to have seen totally unique spectra for this species. It was our wish to attempt to duplicate these experiments with the Fe-Rh/C catalysts. Before the mono-atomic and di-atomic catalysts could be studied, it was necessary to see if this experiment was plausible within the detection limits of the Mössbauer Spectrometer.

A 0.10 wght % Rh (Fe-Rh/C) catalyst was prepared and loaded in the Heli-tran cell. The catalyst had been pre-reduced at 125° in 100 ml·min⁻¹ hydrogen for 2.5 hours prior to introduction into the cell. A spectrum was then taken at 80°K for 10.5 hours while the cell was under vacuum. This spectrum indicated no hyperfine splitting and appeared as a typical Fe-Rh spectrum (See Figure 4.4). This sample was then lowered to 7°K and a spectrum was taken for 12 hours in vacuum (Figure 4.5). The spectrum did not change much which could indicate two possibilities. One, that the particles are so small that no hyperfine field will be evident until lower temperatures are reached, or two, that the iron cannot form a hyperfine field in the alloy because it has been made paramagnetic. This can occur in alloys if the Curie temperature is low enough.

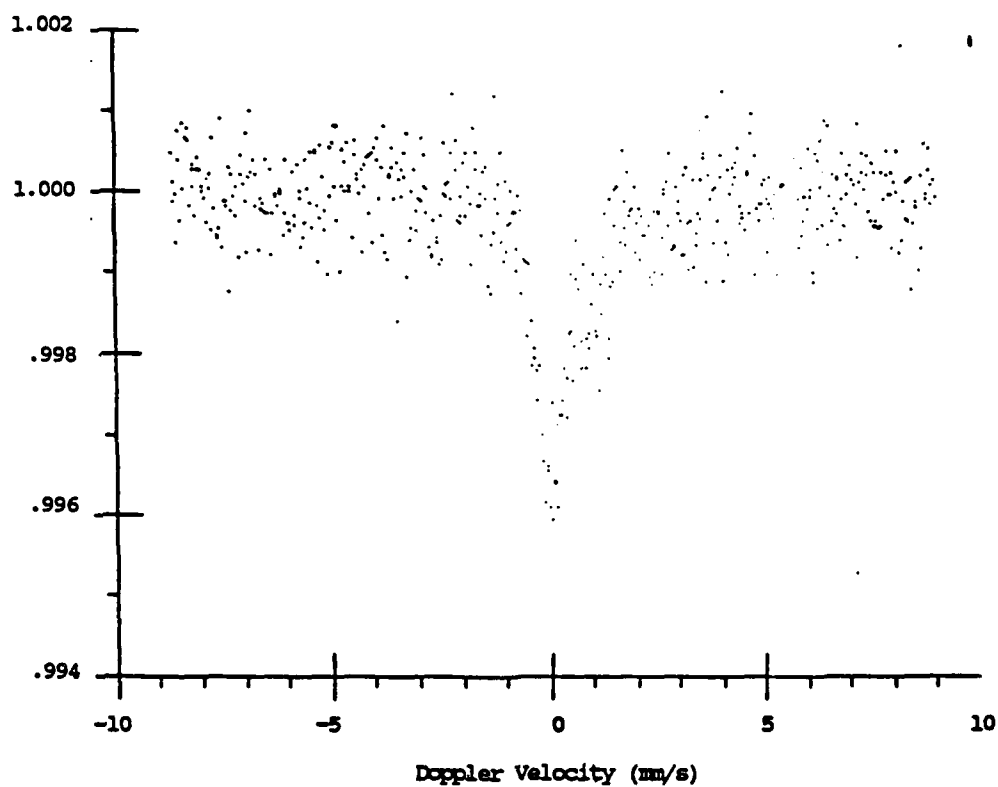


Figure 4.4. Mössbauer Spectrum of 0.10 wght % Rh, Fe-Rh/C Catalyst at 80°K after a 125°C Reduction in Hydrogen.

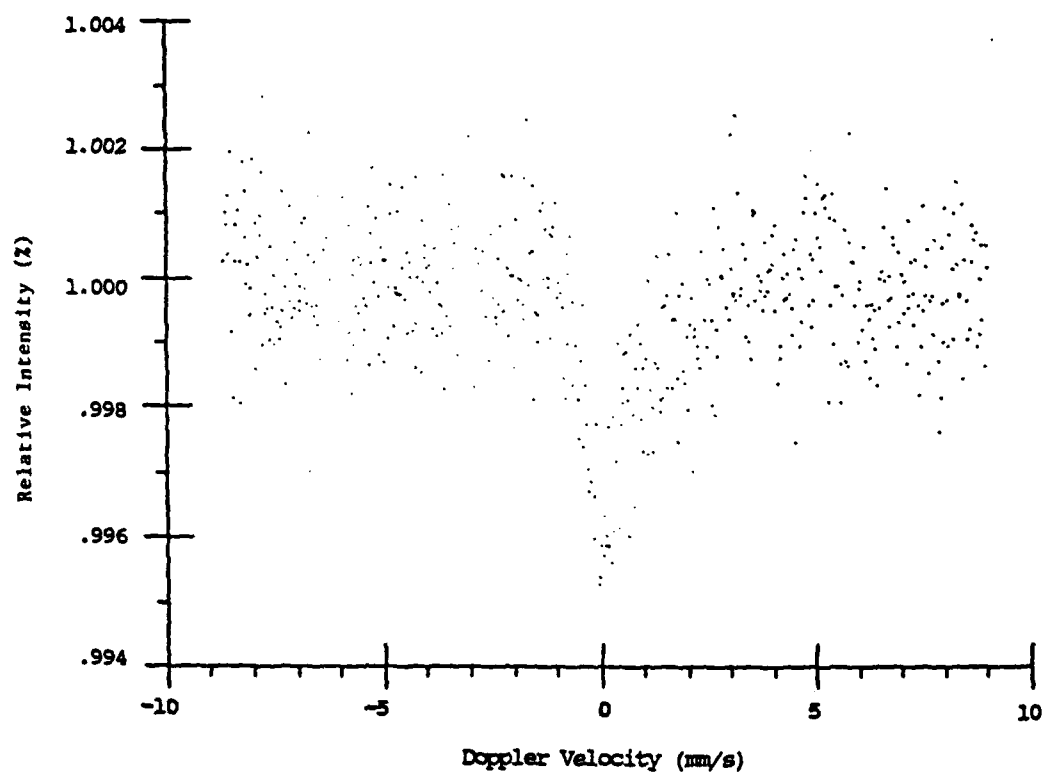


Figure 4.5. Mössbauer Spectrum of a 0.10 wght % Rh, Fe-Rh/C Catalyst at 7.9°K after 125°C Reduction in Hydrogen.

The first possibility was not checked because the cell could not be better shielded, and the pumping capacity necessary to lower the helium temperature by evaporation was not available. Another consideration was the monetary drain that pumping on the helium would create at these collection times.

The second possibility was checked by preparing a Fe/C catalyst from $(CO)_3FeC_7H_8$ on carbon. This catalyst had a 0.06 wght % Fe loading and was reduced and run under the same conditions as the Fe-Rh/C catalyst. The 70K spectrum (Figure 4.6) shows that there is no hyperfine field and that the particles are indeed very small. So, it is not evident whether or not the Fe-Rh/C sample is paramagnetic.

Unfortunately, due to such long collection times, no lower loadings could be studied. The statistics on the fitting program were so inadequate that less signal over a longer time would probably be meaningless. Since at these loadings the Fe-Rh/C catalyst should have particles rather than mono- or di-atomic sites, no further information could be obtained about the diad site. It indicates that, to do a study of this kind, a catalyst enriched with ^{57}Fe must be prepared to give sufficient signal and that the pumping capacity must be increased to further lower the cell temperature.

The other information, however, did not necessarily have to be taken at low loadings. The temperatures needed to achieve complete reduction of the catalyst could be determined with higher loadings. Also, the extent of interaction of the complex could be inferred by

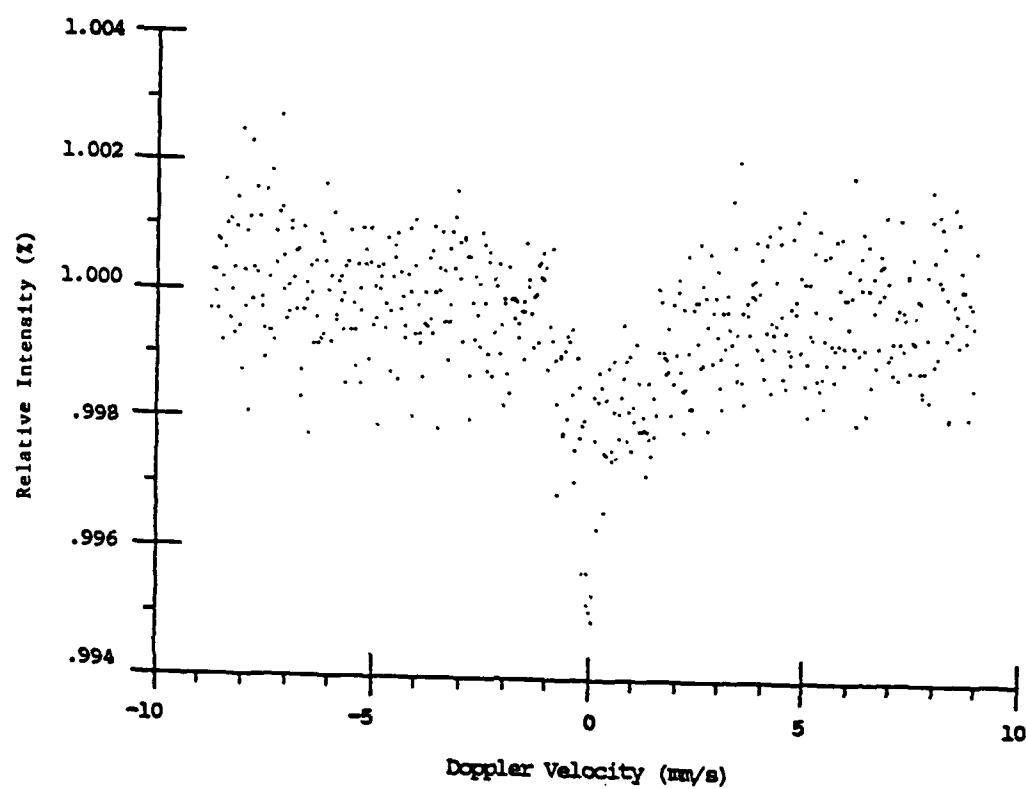


Figure 4.6. Mössbauer Spectrum of a 0.05 wght % Fe/C Catalyst at 7.8°K after 125°C Reduction in Hydrogen.

changes in the spectrum of the complex from solution to support. These investigations were performed and are presented in the following sections.

Interactions of the Complex With the Support

The complex 1 was dissolved in pentane and a spectrum taken of the frozen solution at 80°K under vacuum. The spectrum of the complex in solution appears in Figure 4.7. The spectrum shows an isomer shift consistent with deshielding of the nucleus; the quadrupole splitting indicated that this deshielding was not uniform within the nucleus. A spectrum of complex 1, which had been adsorbed from a pentane solution onto carbon, was taken at room temperature under vacuum (Figure 4.8). Very little interaction occurred between the complex and the support at this temperature. A spectrum taken of this catalyst at 80°K under vacuum shows that the recoil-free fraction had greatly increased (Figure 4.9). This was consistent with a physical adsorption of the complex onto the support.

When the complex was taken up in benzene and adsorbed onto the carbon, the spectrum showed no intensity after 12 hours at room temperature under vacuum meaning the recoil free fraction was very low, and the complex was loosely held on the surface. The spectrum at 80°K (Figure 4.10) demonstrated a much better intensity, but the interaction was weaker than in pentane and showed different isomer shifts and quadrupole splitting parameters. This indicated that both complexes were physically adsorbed on the support, but with

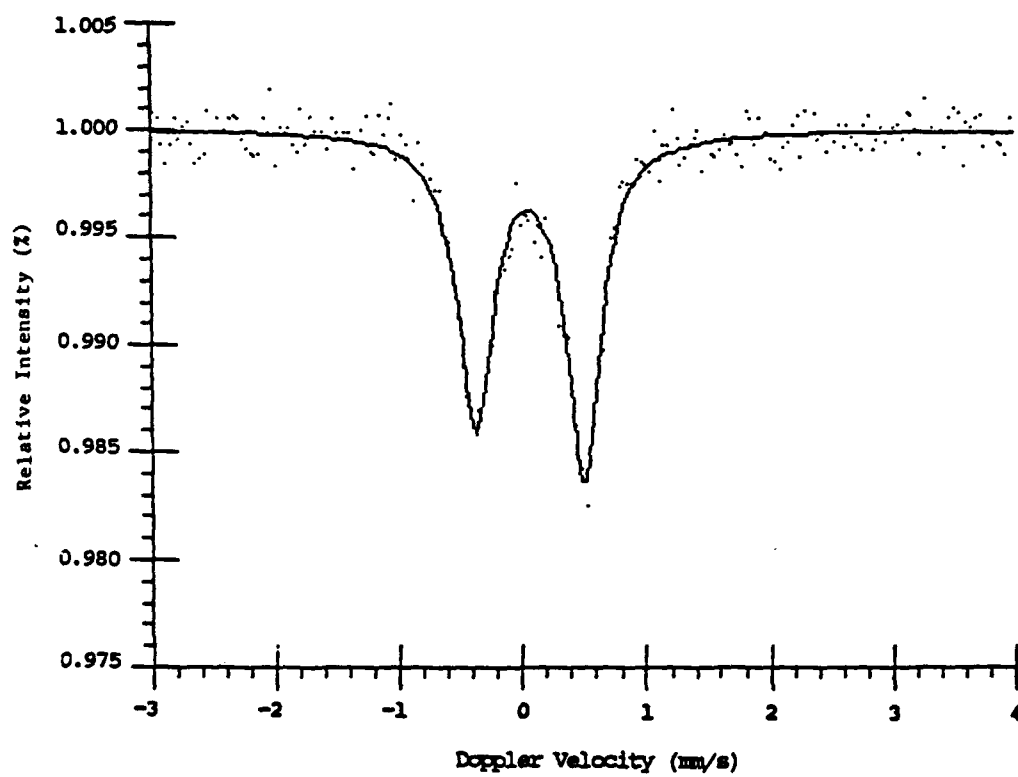


Figure 4.7. $(\text{CO})_3\text{Fe}(\mu\text{-C}_7\text{H}_7)\text{RhCOD}$ Frozen in Pentane at 80°K .

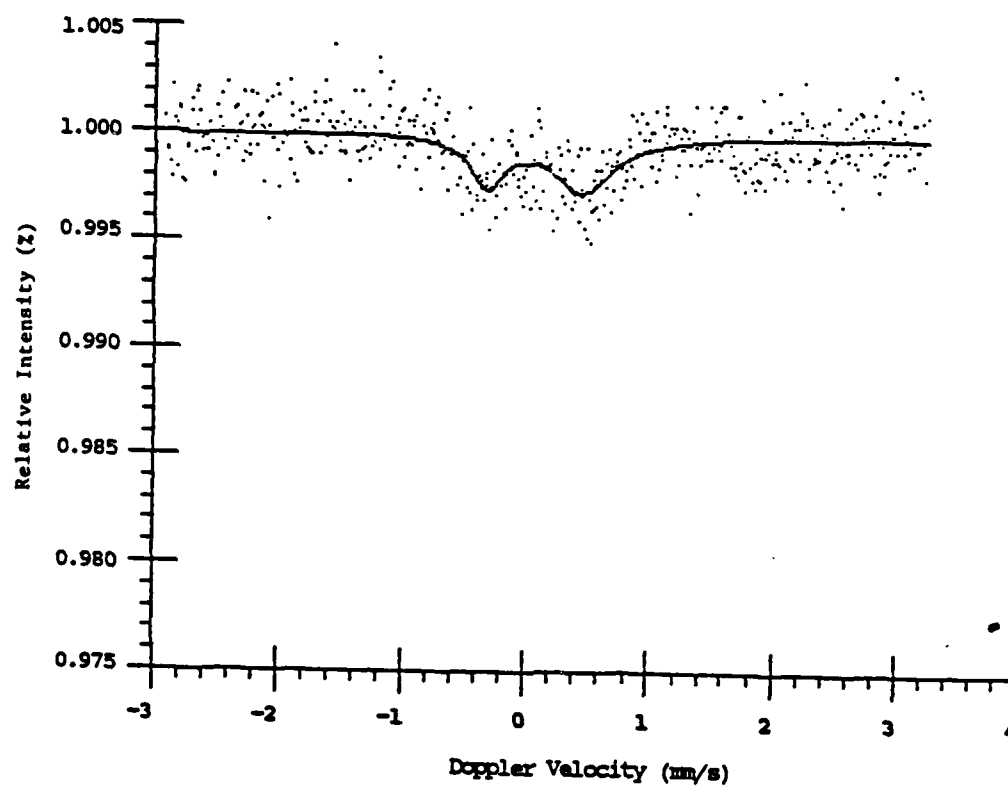


Figure 4.8. Room Temperature Spectrum of 0.39 wght % Rh, Fe-Rh/C-NR Adsorbed on Carbon from Pentane Solvent.

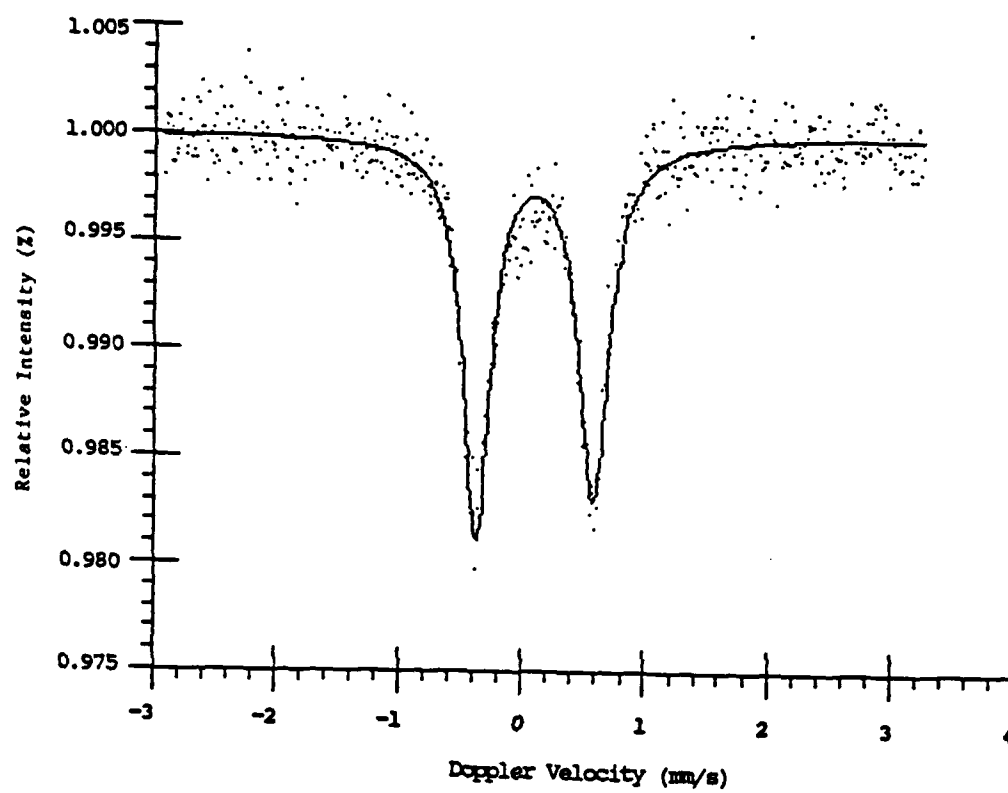


Figure 4.9. Mössbauer Spectrum of 0.39 wght % Rh, Fe-Rh/C-NR₂
Adsorbed on Carbon from Pentane. Spectrum at 80°K.

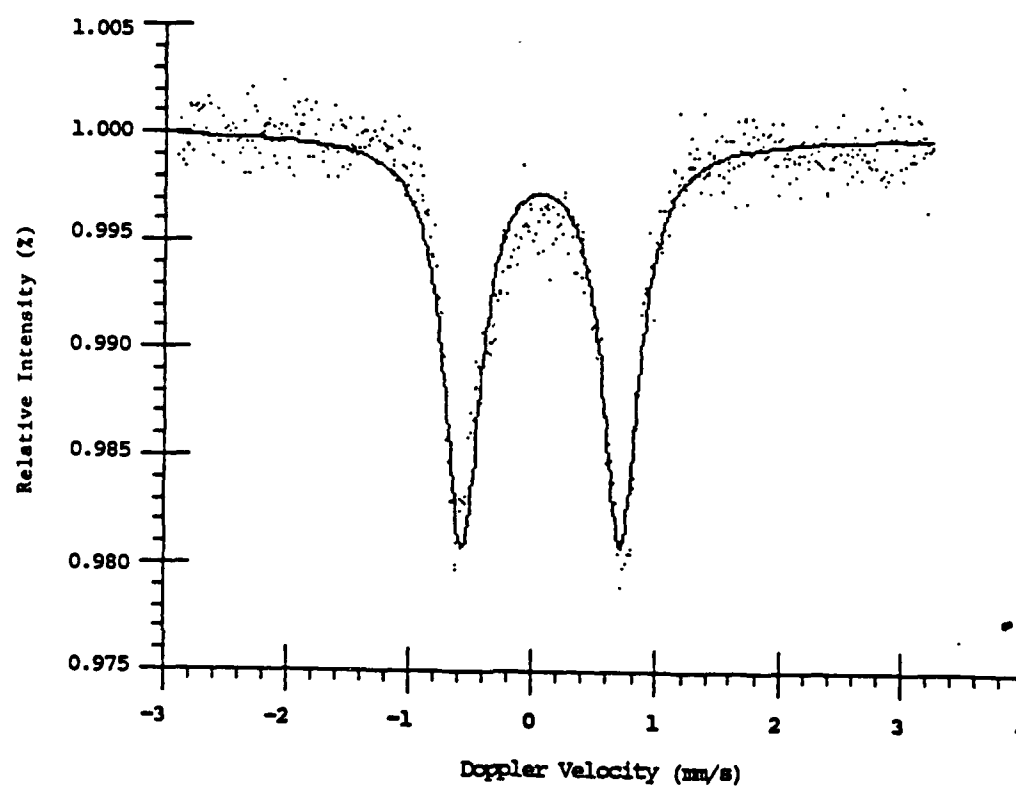


Figure 4.10. Mössbauer Spectrum of 0.39 wght % Rh, Fe-Rh/C-NR
Adsorbed on Carbon from Benzene. Spectrum at 80°K.

different orientations. This could explain the differences in catalytic activity between catalysts prepared in pentane and those in benzene. A summary of the isomer shift and quadrupole splitting parameters appears in Table 4.8.

Determination of Reduction Temperature

The complex 1 was listed as having a decomposition temperature of greater than 100°C.¹⁹ With this in mind, the catalyst (made from complex 1 on carbon using pentane as the solvent) from the previous section was reduced at 125° in flowing hydrogen. The spectrum taken at 80°K under vacuum showed complete reduction of the iron to give a hetero-bimetallic iron-rhodium spectrum (Figure 4.11). After oxidation in air, the complex could be re-reduced in hydrogen at room temperature. These data are consistent with spectra of fully reduced iron rhodium bimetallics prepared using different methods.³⁹

The catalyst prepared from complex 1 in benzene with carbon as the support (previously listed) was also treated under these conditions. It produced a fully reduced iron-rhodium hetero-bimetallic. The spectrum was taken at 80°K under vacuum (Figure 4.12). It was not obvious from the spectrum, taken after reduction, why these catalysts were different. It could indicate that the iron is not influenced by the same factors which influenced the rhodium after catalyst reduction.

Table 4.8

Mossbauer Parameters of Some Fe-Rh/C-NR Catalysts^a

Solvent	Catalyst Preparation	Spectrum Temperature, °K	b	c
pentane	frozen solution	80	0.069	0.885
pentane	adsorbed on carbon	RT	0.076	0.787
pentane	adsorbed on carbon	80	0.096	0.962
benzene	adsorbed on carbon	RT	No Spectrum	
benzene	adsorbed on carbon	80	0.051	1.360

^a All catalysts were a 0.39 wght % Rh, Fe-Rh/C catalyst containing 0.22 wght % Fe. These catalysts were not reduced before the spectra was taken.

^b Isomer shift in $\text{mm}\cdot\text{sec}^{-1}$

^c Quadrapole splitting in $\text{mm}\cdot\text{sec}^{-1}$

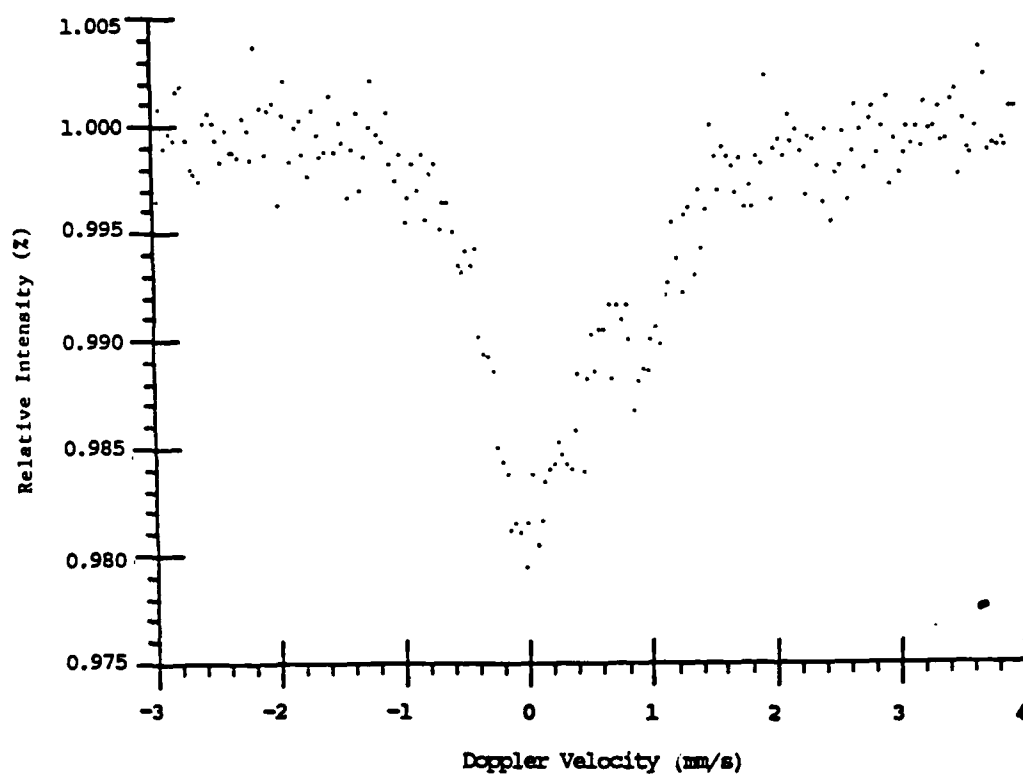


Figure 4.11. Mössbauer Spectrum of Fully Decomposed 0.39 wght % Rh, Fe-Rh/C Catalyst Prepared in Pentane Solvent. Spectrum at 80°K Following 125°C Reduction in Hydrogen.

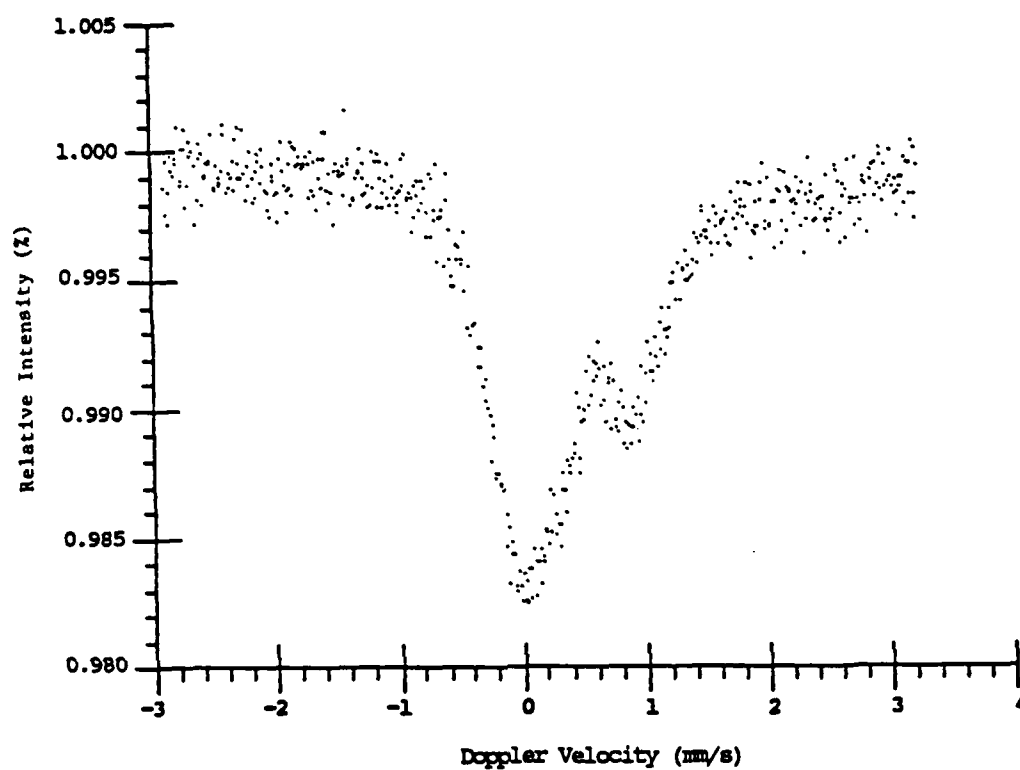


Figure 4.12. Mössbauer Spectrum of Fully Decomposed 0.39 wght % Rh, Fe-Rh/C Prepared from Benzene Solvent. Spectrum at 80°K after 125°C Reduction in Hydrogen.

Effect of Hydrogen on Mössbauer Spectra

During the course of this study there were certain observations made which suggested that spectra of the high loading Fe-Rh/C catalysts taken in hydrogen differed from spectra taken in a vacuum. To properly investigate this phenomenon, a 0.39 wght % Rh, Fe-Rh/C catalyst with 0.22 wght % iron was reduced at 125°C in hydrogen, cooled in a hydrogen atmosphere, and a spectrum taken at 80°K (Figure 4.13). This catalyst was warmed to RT, evacuated for 15 hours, cooled to 80°K, and then another spectrum was taken (Figure 4.14).

Visual inspection revealed that these two spectra were different. The side peak in the bi-metallic spectra almost disappeared in a hydrogen atmosphere, indicating that the presence of hydrogen changes the orientation of the atoms in the particle. This change may be the result of diffusion of hydrogen into the large metal aggregates. If this is the case, it could explain the chemisorption behavior observed with these catalysts. Also, since diads cannot diffuse hydrogen, it may explain the dramatic rate decrease observed by going from a large aggregate to diad sites, by assuming that the metal structure containing hydrogen is a more active catalyst.

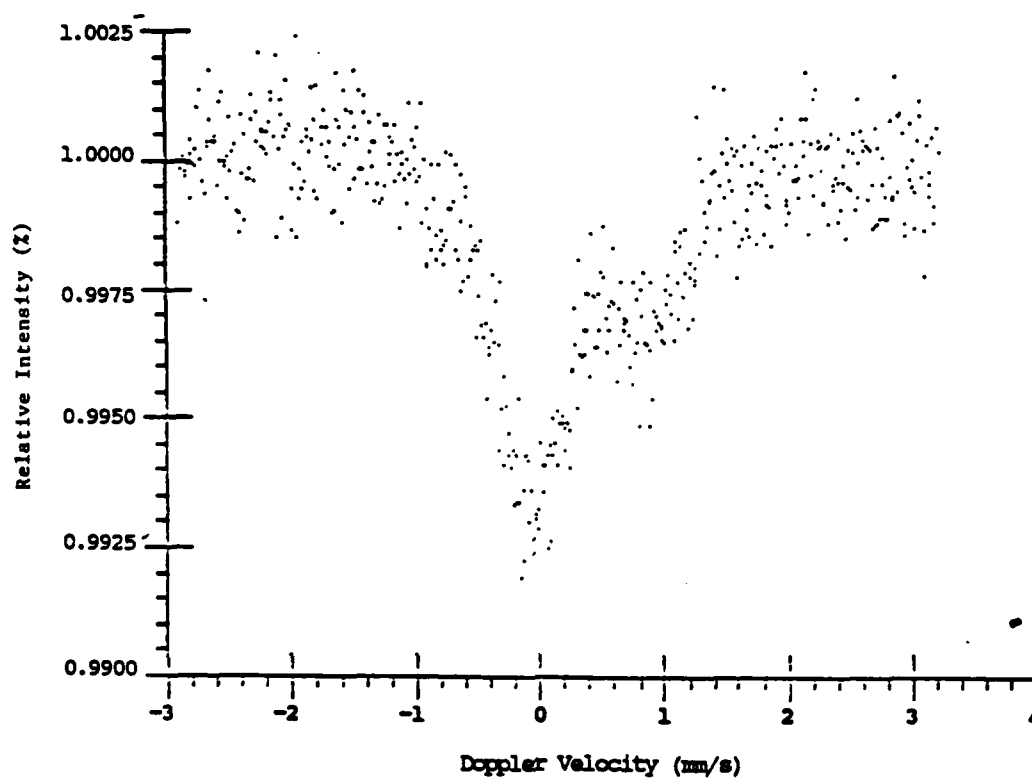


Figure 4.13. Mössbauer Spectrum of a Reduced 0.39 wght % Rh, Fe-Rh/C Catalyst. Spectrum Collected at 20°C in Vacuum.

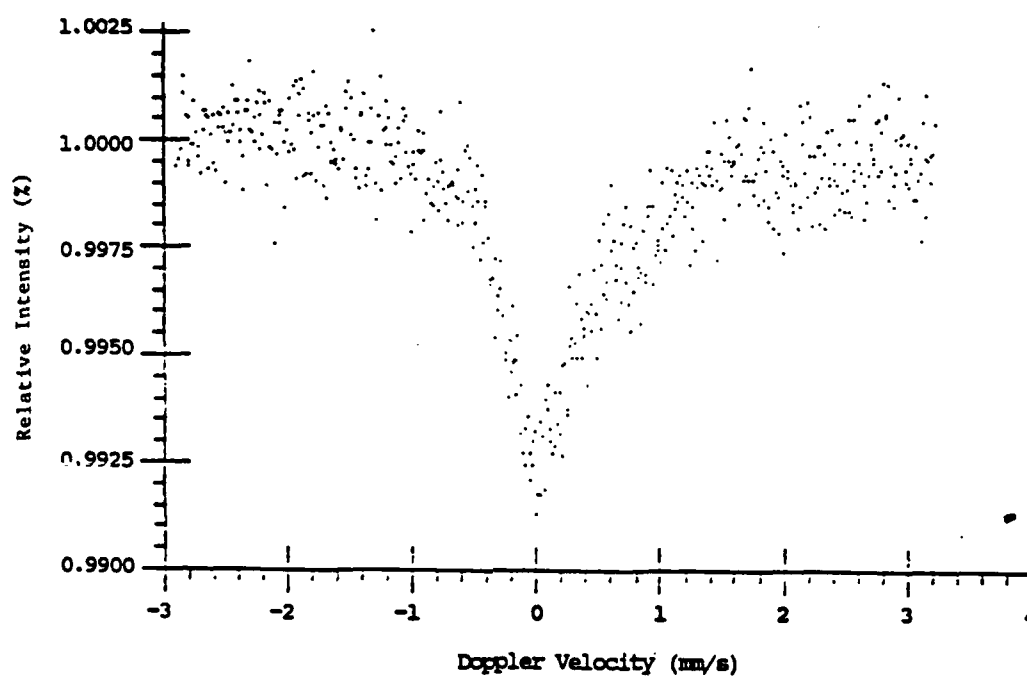


Figure 4.14. Mössbauer Spectrum of a Reduced 0.39 wght % Rh, Fe-Rh/C Catalyst. Spectrum Collected at 20°C in Flowing Hydrogen.

Chapter V

CONCLUSION

This study clearly demonstrates that a new type of catalyst can be prepared having an iron-rhodium diad as the active site. These catalysts exhibit new properties never before attributed to this metal combination. They also exhibit properties different from either isolated atom. These diad sites can interact with a carbon support to a much greater degree than can metal aggregates. These interactions may modify the diad's catalytic properties in a manner analogous to varying the ligands in a homogeneous catalyst. These observations may be extended to various supports in a similar manner. However, these catalysts are sensitive to the method of preparation, and the parameters of preparation should be thoroughly investigated for each precursor.

The rhodium on alumina catalysts cannot be isomerization catalysts because rhodium atoms are deactivated on alumina supports. The rhodium atoms may be deactivated by surface sites or may ionize and diffuse into the alumina matrix. Investigators have not observed rhodium atoms with their various methods of characterization because the metal loadings of the catalysts they investigated were too high.

The Mössbauer Effect can be used to investigate adsorbed species on a carbon support. The investigation of these new sites, however, must be carried out with a ^{57}Fe enriched catalyst

to attain the required sensitivity. If this is done, this characterization method could become a powerful tool for investigation of catalytic surfaces.

Chapter VI

FUTURE RECOMMENDATIONS

New mono- and di-atomic site catalysts should be prepared with different metals and metal combinations. These should then be investigated to see if they will catalyze other reactions. The catalysts should also be prepared on various supports to determine the effect of each support. Various reactions which currently must be performed under homogeneous conditions should be tested for adaptation to heterogeneous systems. The surface properties of semiconductors may be altered specifically and uniformly with these new sites. Specific experiments could determine if these new catalysts will act as more efficient fuel cell catalysts.

The Mössbauer Effect should be used to investigate these sites with ^{57}Fe . Also, the hydrogen chemisorption differences between large particles and these new sites should be determined. This would lead to new explanations of the mechanism by which heterogeneous catalysts function.

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